

## A Closed Tube Method for Measuring Gas Diffusion Coefficients

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### ABSTRACT

A transient, closed tube method for measuring both ordinary gas diffusivities and porous media effective diffusivities is presented. The current method is suitable for measuring gas diffusivities in air-dry systems over a range of temperatures. Gas concentrations are continuously monitored in a well-stirred volume of a single end chamber, which is connected to a closed sample chamber during experiments. An analytic solution for this diffusion process is available in which, after a sufficient time, the diffusivity of the sample is obtained from the slope of the logarithm of dimensionless concentration excess versus time. The method was checked by comparing measurements of N<sub>2</sub>-O<sub>2</sub> gas diffusivities at 0, 30, and 60 °C to various previously reported values in the literature. The measured diffusivities fall within the uncertainties of these earlier works.

**Additional Index Words:** Fick's law, effective diffusivity, temperature-dependence, O<sub>2</sub> diffusion.

**G**AS DIFFUSION through soil and rock systems is a transport mechanism associated with a variety of processes. In soil science, gas diffusion has long been recognized as an important mechanism for soil gas exchange with the atmosphere. Numerous soil chemical, pedogenic, microbial, and plant related processes are closely associated with the diffusive transport of O<sub>2</sub>, CO<sub>2</sub>, and various forms of N. Gas diffusion in soil is of environmental concern in the case of leakage of CH<sub>4</sub> and other hydrocarbons through soil covers overlying waste disposal sites. More recently, interest in understanding gas diffusion through soil and rock has grown due to realization that diffusion is potentially a major pathway for radioactive gas transport. This concern is associated with both Rn gas transport in the natural environment as well as gas transport out of radioactive waste repositories. Radon gas transport studies have been directed at leakage from U tailings piles and problems of indoor air quality in housing. The migration of various gaseous radionuclides such as <sup>129</sup>I, <sup>14</sup>C, and <sup>85</sup>Kr away from proposed high-level nuclear waste repositories is of increasing concern (Roseboom, 1983). These gases, along with others, are expected to be released from high-level waste canisters as they inevitably deteriorate.

In each of the aforementioned areas of interest in gas diffusion, a range of temperatures can prevail. For surface soils, this range may be about ± 30 °C. Models of high level nuclear waste repositories predict temperature increases of > 100 °C at repository boundaries (Klasi et al., 1982). The temperature dependence of gas diffusion in porous media is therefore of interest in all of these processes.

Gas diffusion in soils and other porous media is

generally described through various forms of Fick's laws of diffusion (e.g., Hillel, 1980). The local diffusive gas flux density  $q_d$  is given by Fick's first law as

$$q_d = -D_c (\partial c / \partial x) \quad [1]$$

where  $\partial c / \partial x$  is the local concentration gradient, and the proportionality constant  $D_c$  is the porous medium effective diffusivity. The conventional approaches to characterizing  $D_c$  used in soil science involve scalar reductions of ordinary gas diffusion coefficients,  $D_o$ , due to effects of gas porosity,  $\epsilon_g$ , and tortuosity (e.g., Troeh et al., 1982). In a one-dimensional homogeneous system, the local time-dependence of concentration in the absence of sinks or sources is given by Fick's second law

$$\frac{\partial c}{\partial t} = \frac{D_c}{\epsilon_g} \frac{\partial^2 c}{\partial x^2} \quad [2]$$

which results from combining Fick's first law with the continuity equation. In both of the above equations, an understanding of the nature of  $D_c$  is required in order to proceed with predictions of diffusive fluxes. In order to predict the temperature-dependence of gas diffusion in the environment, it is essential to understand the effects of temperature on  $D_c$ .

A new method for measuring both ordinary gas diffusivities as well as porous media effective diffusivities is presented here. This method is suited for measuring gas diffusivities over a range of temperatures. Before proceeding to describe the method and results, a brief overview of some existing laboratory methods for measuring  $D_c$  will be provided. The various methods will be grouped into categories, which have been previously been used by Marrero and Mason (1972). This survey will lead to the motivation for developing a new method for measuring  $D_c$ .

Laboratory methods for measuring gas diffusion coefficients in porous media may be categorized into steady-state and transient methods. Examples of methods include those by Penman (1940), and Van Bavel (1952, in which a correction to Penman's method is also noted). One-dimensional transient methods can be divided into open tube and closed tube methods. In open tube methods, one end of the sample porous medium is open to either the atmosphere or some other very large volume of gas, effectively establishing a constant concentration boundary condition. The methods of Taylor (1949), Currie (1960), Papendick and Runkles (1965), and Bakker and Hidding (1970) are in this category. A generalization of this open tube approach, in which imposed time-dependent boundary gas concentrations are used, is given by Rolston and Brown (1977). In both steady-state and transient open tube methods, at least one boundary of the porous medium must be connected to a large reservoir of gas.

Closed tube methods generally utilize information on the time-dependent gas concentration changes at one or two sealed end chambers in contact with the porous sample to calculate  $D_c$ . The sample is open

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only to the end chamber(s); thus the closed tube systems are isolated from the atmosphere. Closed tube methods have several advantages over both steady-state and open tube methods. In closed systems, hazardous or expensive gases can be contained and conserved. Closed systems are relatively easily adapted to experiments at total pressures other than atmospheric pressure. Finally, a closed system can be placed in a temperature-regulated bath for greater temperature control.

Several transient, closed tube methods have been available. In single end chamber methods, only one end of an otherwise closed sample chamber is exposed to an end chamber with which gas exchange occurs. Rust et al. (1957) have presented a single end chamber method. Their approach is constrained by the analytic solution used, due to Scott et al. (1951), to sample end chambers of equal lengths and areas. Furthermore, gas transport must be purely diffusive within both chambers. Several dual end chamber methods have also been developed. Dual end chamber methods consist of a sample column with opposite ends joinable to otherwise closed end chambers. The dissipation of initially imposed gas concentration differences can be monitored at either one or both end chambers. The methods of Ball et al. (1981), Reible and Shair (1982), and Sallam et al. (1984) are dual end chamber approaches.

In the following sections, a new method for measuring gas diffusivities over a range of temperatures is presented. The use of a closed system was preferred due to ease of temperature regulation by submersion in a controlled-temperature water bath. A single end chamber method was preferred over a dual end chamber system due to the simplicity of the former. Finally, in light of the observations by Currie (1960) of end chamber convection even in the absence of active mixing, the single end chamber, closed tube method developed by Rust et al. (1957) appeared unsatisfactory. Thus, the combination of features sought for diffusivity measurements over a range of temperatures led to the development of a new single end chamber, closed tube method in which end chamber mixing was

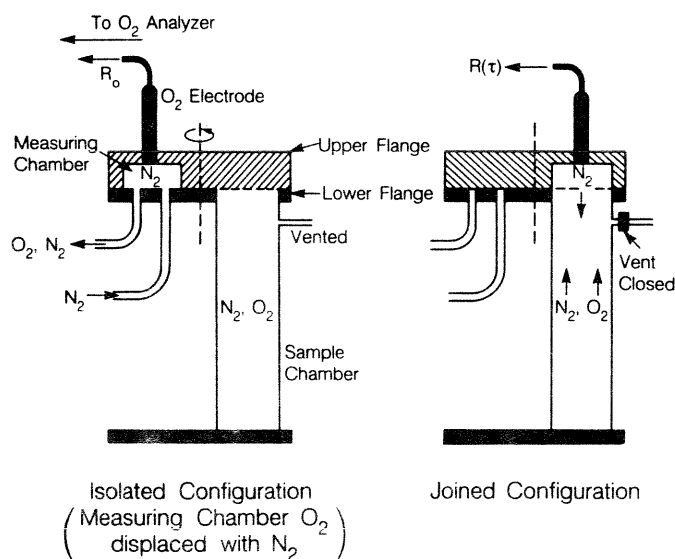


Fig. 1. Diffusion cell.

accommodated. In the following sections, the diffusion cell is described, the use of an analytic solution is outlined, and  $N_2$ - $O_2$  gas diffusivity measurements made with this new method are presented. The measured ordinary gas diffusivities are compared with previously reported data obtained by others in order to check the applicability of the new method.

## Methods

### Diffusion Cell Design

To allow measurement of  $D$ , at a variety of temperatures, a diffusion cell that could be immersed in a temperature-regulated water bath was desired. In the diffusion cell developed by Currie (1960), one end of the sample chamber was open to atmospheric air, a condition prohibited by the requirement of a water bath. The method developed for the current study is essentially a modification of Currie's design. The basic features of the new diffusion cell are depicted in Fig. 1 and 2. It consists of two chambers that can be joined end to end or isolated from each other. The lower chamber contains the sample of interest in a 0.204-m Al tube, with a closed bottom. For measuring ordinary gas diffusivities, a bundle of open-ended stainless steel tubes was inserted into the lower chamber. The 8.13-mm o.d., 9.53-mm o.d. tubing served to minimize convective mixing within the otherwise empty sample chamber. The top end of the sample chamber is covered with a sheet of filter paper (Whatman no. 1) and coarse-mesh screen. The open upper end of the sample chamber is inserted into the lower flange. The upper chamber is referred to as the measuring chamber since gas composition is measured in a sampling loop connected to this chamber. The measuring chamber can be either isolated from or joined with the sample chamber by rotation of the lower flange relative to the upper flange. Oxygen gas served as the diffusing species to be monitored in our work. The method appears suited for use with other gases as well. Prior to a

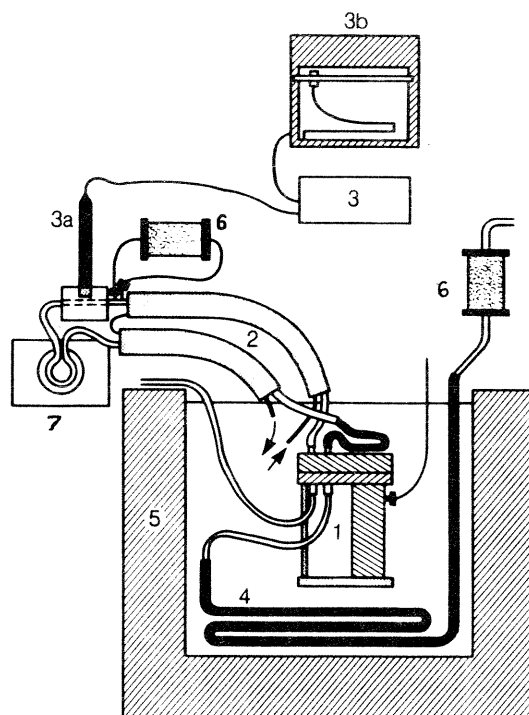


Fig. 2. Diffusion cell and supporting equipment. (1) Diffusion cell, (2) measuring chamber loop, (3) oxygen analyzer, (3a) oxygen electrode, (3b) chart recorder, (4) nitrogen reservoir, (5) insulated water bath, (6) desiccators, and (7) peristaltic pump.

set of experiments, atmospheric air was allowed to fill the sample chamber gas volume. This provides an initial  $O_2$  mole fraction of about 0.209 in the sample's gas phase, which was equilibrated with local atmospheric pressure. Due to the strong dependence of gas diffusion on total pressure, the local atmospheric pressure is measured with a Hg barometer at the beginning and end of each experiment. The two chambers are initially isolated from each other so that  $N_2$  gas could be flushed through the measuring chamber to provide an initially lower  $O_2$  concentration. The choice of lowering the  $O_2$  concentration within the upper (measuring) chamber rather than in the lower (sample) chamber for establishing initial conditions was deliberate. Since  $O_2$  is of higher molecular weight than  $N_2$ , buoyant mixing effects are prevented in the chosen procedure. At the beginning of an experiment, the two chambers are joined, allowing  $O_2$  to diffuse upwards into the measuring chamber (while  $N_2$  diffuses downward). The  $O_2$  concentration in the measuring chamber is continuously monitored until a new equilibrium is established.

Oxygen concentrations within the measuring loop were continuously monitored with a Beckman model 0260 polarographic electrode and analyzer. The oxygen analyzer output signal was recorded on a strip chart recorder. The gas within the loop is continuously circulated by a peristaltic pump at a rate of  $1.7 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ . The loop gas circulates into and out of the upper flange chamber, which is submerged (with the sample chamber) in the temperature bath. The loop tubing, which extends out of the bath, is kept at the bath temperature by circulation of water from the bath through jackets covering the gas loop tubing. The oxygen electrode is inserted into the measuring loop outside of the temperature bath. Most of the loop's length consisted of 5.00-mm i.d., 6.35-mm o.d. copper tubing.

Both the measuring chamber loop and sample chamber can be equilibrated with atmospheric pressure through closable vents. The vents connect the chambers to the atmosphere through about 1-m lengths of surgical tubing. This tubing allows for rapid total pressure equilibration while impeding diffusive exchanges with the external environment. When the system is undergoing thermal equilibration, the vents are left open to keep pressures equal to atmospheric pressure. Just prior to the beginning of experiments, the vents were closed to isolate the system from the environment. At the end of each experiment, the sample chamber was briefly vented to verify that atmospheric pressure has been maintained during the course of the experiment. When this condition was met, no sudden deflection in the  $O_2$  analyzer output was observed upon venting. Analyzer responses are due to the fact that the  $O_2$  electrode potential reflects the free energy of  $O_2$ , a function of total pressure as well as  $O_2$  partial pressure.

The  $N_2$  gas was thermally equilibrated prior to entry into the measuring chamber loop. Thermal equilibration was accomplished by placement of a  $N_2$  reservoir in the temperature bath. The reservoir is a coil of 7.90-mm i.d., 9.53-mm o.d. copper tubing chosen to facilitate heat exchange.

For diffusion experiments performed at  $60^\circ\text{C}$ , small amounts of water vapor occasionally were observed to condense on the oxygen electrode tip, resulting in distortion of the electrode output. The desiccator columns shown in Fig. 2 were included to remove excess water vapor prior to performing diffusion experiments. One desiccator column is located on the inlet end of the  $N_2$  reservoir to keep the purging gas dry. Thus, the incoming gas is both dried and thermally equilibrated prior to entry into the diffusion cell. The other desiccator is attached to the diffusion cell by tapping into the measuring chamber loop. Prior to a set of experiments on a given day, the sample chamber was joined with the measuring chamber loop for drying of the whole system. After drying (at the experimental temperature), the loop desiccator is removed, and the system is closed in preparation

for beginning experimentation. The use of desiccators is unnecessary for  $O_2$  diffusion experiments performed at or below room temperature. Due to the problem of water condensation at the oxygen electrode, the particular design presented here can not be used with moist soils above room temperature. The use of alternative gas analyzing methods and other tracer gases may circumvent the need to predry gases and permit more general use of this method with moist soils.

The temperature control system consists of an insulated water bath, a 200-W heating coil, a temperature regulator and thermistor, and a water circulating pump. The pump not only stirs water in the bath but cycles water through the previously described measuring loop jackets as well. The temperature regulator, thermistor, and heating coil are used for experiments conducted above room temperature. For  $0^\circ\text{C}$  experiments, the water bath is filled with a slurry of water and crushed ice. Temperatures were monitored in both the water bath and the return-flow outlet of the measuring loop water jacket. A preliminary thermal equilibration test with a thermistor inserted into the center of the tubing bundle in the sample chamber demonstrated that only about 30 min was required to raise the core temperature to  $60^\circ\text{C}$ . All experiments were conducted at temperatures within  $\pm 0.1^\circ\text{C}$  of selected temperatures.

### Analytic Solution to the Diffusion Process

The physical conditions described in the previous section will now be abstracted into initial and boundary conditions, for which the diffusion equation is solved. The experimental conditions impose one-dimensional (vertical) diffusion within the sample chamber of length  $L$ . The lower end of the sample (at  $x = 0$ ) is characterized by an impermeable boundary condition. The sample is characterized by its diffusivity  $D_c$  and porosity  $\epsilon_c$ . In the case of ordinary diffusivity ( $D_o$ ) measurements, the measured  $D_c$  is equatable to  $\epsilon_c D_o$ , where  $\epsilon_c$  is the gas porosity of the steel tubing bundle inserted into the sample chamber. This simple relation between  $D_c$  and  $D_o$  results from the fact that the tortuosity factor for the tubing bundle along the  $x$  axis is unity. Thus, the diffusive flux density within the sample chamber is hindered to the extent that only the fraction  $\epsilon_c$  of the sample cross-sectional area is available for transport. The sample chamber cross-sectional area is designated  $A$ . The upper end of the sample (at  $x = L$ ) is characterized by a well-stirred volume. The volume of the measuring chamber and loop is equal to the product  $a \cdot A$ , thus the equivalent length of the measuring chamber/loop is  $a$ . The sample pore gas has an initial concentration of  $O_2$  denoted  $C_{s0}$ . The initial gas concentration of  $O_2$  in the measuring chamber/loop is  $C_0$ . These boundary and initial conditions are depicted in Fig. 3.

The partial differential equation describing conservative, isothermal, isobaric, one-dimensional binary gas diffusion in a homogeneous porous system, Eq. [2], applies to the region  $0 \leq x \leq L$ . Effectively instantaneous transport governs the region  $L \leq x \leq (L + a)$ . The initial conditions are

$$C(x, 0) = C_{s0} \quad 0 \leq x \leq L \quad [3a]$$

$$C(x, 0) = C_0 \quad L \leq x \leq L + a. \quad [3b]$$

The boundary conditions are

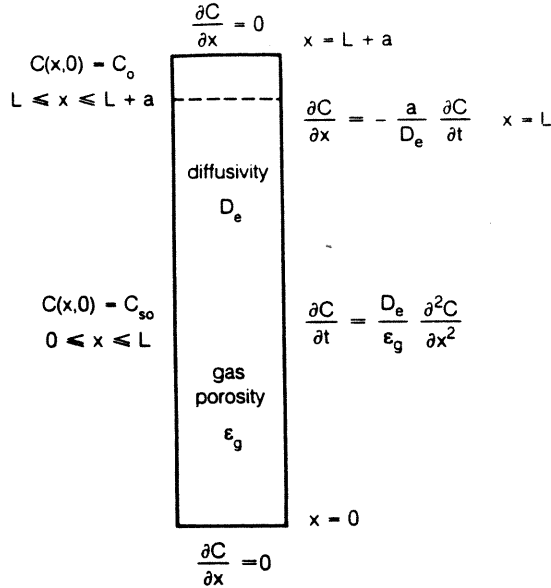
$$\frac{\partial C}{\partial x} = 0 \quad x = 0 \quad [4a]$$

$$\frac{\partial C}{\partial x} = -\frac{a}{D_c} \frac{\partial C}{\partial t} \quad x = L \quad [4b]$$

$$\frac{\partial C}{\partial x} = 0 \quad x = L + a. \quad [4c]$$

The solution of the analogous heat conduction problem is given in Carslaw and Jaeger (1959, p. 128). Substituting the appropriate parameters, the solution to Eq. [2], subject of Eq. [3] and [4] is

$$\frac{C(x, t) - C_{so}}{C_o - C_{so}} = \frac{a}{a + \epsilon_g L} \quad [5]$$



$$\frac{C(x, t) - C_{so}}{C_o - C_{so}} = \frac{a}{a + \epsilon_g L} + \frac{2\epsilon_g}{a} \sum_{i=1}^{\infty} \frac{\cos(\beta_i x) \exp(-D_e \beta_i^2 t / \epsilon_g)}{\cos(\beta_i L) \{L[\beta_i^2 + (\epsilon_g/a)^2] + (\epsilon_g/a)\}}$$

where  $\beta_i$  are the roots to

$$\beta_i L \cot(\beta_i L) = -\frac{\epsilon_g L}{a}$$

Fig. 3. Initial and boundary conditions for diffusion experiments.

$$+ \sum_{i=1}^{\infty} \frac{2\epsilon_g \cos(\beta_i x) \exp(-D_e \beta_i^2 t / \epsilon_g)}{a \cos(\beta_i L) \{L[\beta_i^2 + (\epsilon_g/a)^2] + (\epsilon_g/a)\}}$$

where  $\beta_i$  are the roots to

$$\beta_i L \cot(\beta_i L) = -(\epsilon_g L/a). \quad [6]$$

At  $x = L$ , Eq. [5] simplifies to

$$\Gamma(t) - B = \frac{2\epsilon_g}{a} \sum_{i=1}^{\infty} \frac{\exp(-D_e \beta_i^2 t / \epsilon_g)}{L[\beta_i^2 + (\epsilon_g/a)^2] + (\epsilon_g/a)}, \quad [7]$$

where

$$\Gamma(t) = \frac{C(L, t) - C_{so}}{C_o - C_{so}} \quad [8a]$$

and

$$B = \frac{a}{a + \epsilon_g L}. \quad [8b]$$

Eq. [7] applies at all times and positions within the measuring chamber/loop,  $[L < x \leq (L + a)]$ , due to the well-stirred boundary condition.

After a sufficient time (discussed in the Appendix), Eq. [7] simplifies further to

$$\Gamma(t) - B = I \exp(-D_e \beta_1^2 t / \epsilon_g), \quad [9]$$

where

$$I = 2\{aL \epsilon_g^{-1} [\beta_1^2 + (\epsilon_g/a)^2] + \}^{-1}, \quad [10]$$

which is again valid within the measuring chamber/loop. Thus, after a sufficient time the effective porous media gas diffusivity is obtainable from the slope of a plot of  $\ln(\Gamma - B)$  vs. time. Specifically,

$$D_e = -\frac{\epsilon_g}{\beta_1^2} \frac{d}{dt} \ln(\Gamma - B), \quad [11a]$$

which in the case of ordinary gas diffusion through the tubing bundle becomes

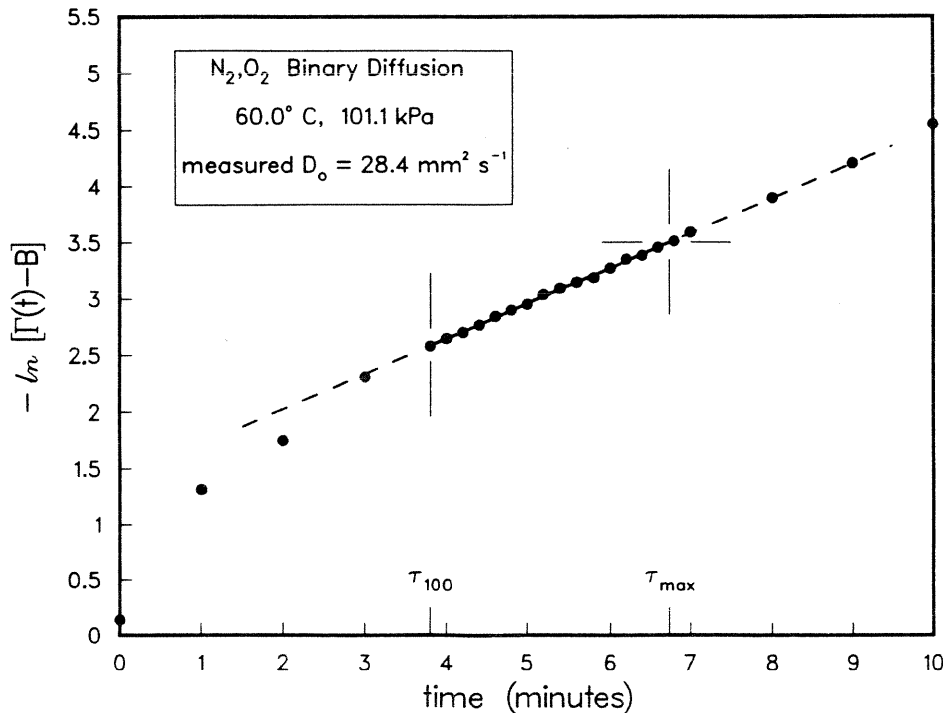


Fig. 4. Plot from a single diffusion experiment.

$$\epsilon_g D_o = -\frac{\epsilon_g}{\beta_1^2} \frac{d}{dt} \ln(\Gamma - B). \quad [11b]$$

Thus, for ordinary gas diffusivity measurements,  $D_o$  is obtained by dividing the above equation by  $\epsilon_g$  of the steel tube bundle.

The gas-filled porosity,  $\epsilon_g$ , is obtained through Eq. [5] (or Eq. [7] or [9]) in the equilibrium limit where

$$\lim_{t \rightarrow \infty} \left[ \frac{C(L, t) - C_{so}}{C_0 - C_{so}} \right] = \frac{a}{a + \epsilon_g L} \quad [12a]$$

$$\epsilon_g = \frac{a}{L} \left[ \frac{C_{\infty} - C_0}{C_{so} - C_{\infty}} \right] \quad [12b]$$

with  $C_{\infty}$  being the  $O_2$  concentration upon reaching diffusive equilibrium.

The  $a$  dimension can be calculated from the above result when  $\epsilon_g$  is predetermined. Although the sample chamber length  $L$  is easily measured directly with a ruler, the effective length  $a$  of the measuring chamber/loop can only be indirectly measured due to its complex geometry. Three parameters,  $\epsilon_g$ ,  $L$ , and  $a$ , effectively determine the relative gas phase volumes associated with the sample chamber and measuring chamber/loop. By rearranging Eq. [12b], measures of the  $a$  dimension are obtained at the end of diffusion experiments when  $L$ ,  $\epsilon_g$ , and the initial and final gas concentrations are known.

$$a = \epsilon_g L \left[ \frac{C_{so} - C_{\infty}}{C_{\infty} - C_0} \right]. \quad [12c]$$

Alternative solutions to Eq. [2] subject to conditions [3] and [4] are provided in Crank (1975). One of these is suitable for short times, while the other is suited for very small

values of  $a/\epsilon_g L$ . Diffusion coefficients could also be deduced from computer curve fitting of all data points up to time  $\tau_{\max}$  (defined in the Appendix).

## RESULTS AND DISCUSSION

$D_o$  for  $N_2$ - $O_2$  diffusion were measured at 0, 30, and 60 °C. Experiments were performed at local atmospheric pressures. Individual experimental data sets of  $O_2$  concentration vs. time were transformed into logarithms of dimensionless concentration excess vs. time, as shown in Fig. 4.  $D_o$  values were obtained from slopes of these functions through Eq. [11]. Slope analyses were performed on data within the time range bounded by  $\tau_{100}$  and  $\tau_{\max}$ . These time parameters are discussed in the Appendix. Measured  $D_o$  values are presented in Table 1.  $N_2$ - $O_2$  diffusivities reported by other workers are given in Table 2. The present measurements and earlier results are compared in Fig. 5. Linear regressions of present and previous data are included for comparison. In this figure, the present results have been normalized to standard atmospheric pressure,  $P_o$  (101.3 kPa). This normalization involved multiplying the measured diffusivity by the ratio  $P_o/P$ , where  $P$  is the absolute pressure under which the particular experiment was performed. The ratio accounts for the inverse dependence of  $D_o$  on  $P$ , and cancels any differences between individual measurements, which are due to differences in the ambient barometric pressure. Also plotted on Fig. 5 is the regression equation

$$D_o = \frac{P_o}{P} (1.13 \times 10^{-3}) T^{1.724} \quad (\text{mm}^2 \text{ s}^{-1}) \quad [13]$$

Table 1.  $D_o$  measurements for  $N_2$ - $O_2$  (adjusted 101.3 kPa).

$T$ °C	$D_o$ mm <sup>2</sup> s <sup>-1</sup>	CV %	$\bar{D}_o$ mm <sup>2</sup> s <sup>-1</sup>	CV of $\bar{D}_o$ %
0.0	18.6	1.7	18.9	5.5
	17.4	1.1		
	20.1	1.5		
	19.0	1.6		
	18.2	1.4		
	20.0	0.6		
30.0	24.5	0.9	22.2	5.8
	21.4	2.0		
	21.1	1.1		
	21.3	1.4		
	22.8	2.1		
	22.3	1.5		
60.0	26.9	1.4	27.7	3.2
	27.2	1.9		
	28.3	1.9		
	27.7	2.2		
	26.9	1.2		
	28.9	1.8		

Table 2.  $N_2$ - $O_2$   $D_o$  data (at 101.3 kPa).

$T$ , °C	$D_o$ , mm <sup>2</sup> s <sup>-1</sup>	Reference source
11.7	20.5	Jackmann, 1906
13.1	20.2	
20	22	Waldmann, 1944
25	17.1	Giddings and Seager, 1962
25	23	Arnikar et al., 1967
27	20.8	Weissman and Mason, 1962
40	21.7	Saxena and Gupta, 1970
40	22.4	
51	26.0	Bohemen and Purnell, 1961
51	26.7	

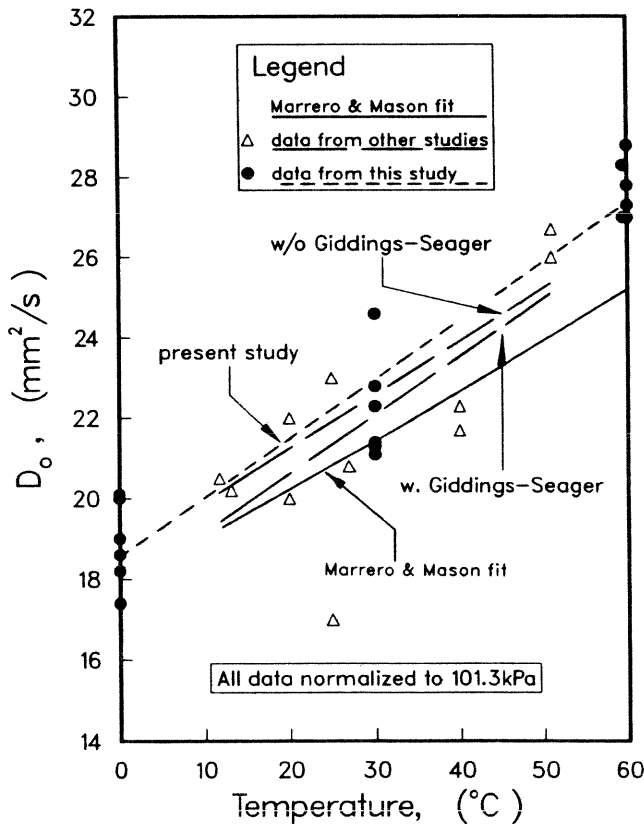


Fig. 5. Comparison of  $N_2$ - $O_2$   $D_o$  measurements reported in this study and in previous works (refer to Tables 1 and 2).

for  $N_2$ - $O_2$  diffusion suggested by Marrero and Mason (1972). In the above equation,  $P_o$  is the standard atmospheric pressure, and  $P$  and  $T$  are the absolute pressure and Kelvin temperature for the system of interest. Equation [13] was generated from a sparse set of  $D_o$  measurements spanning a very wide range of temperatures from 285 (12 °C) to 10 000 K.

Individual experiments provided well-defined slopes, from which  $D_o$  were calculated (Fig. 4). Coefficients of variation, CV, for single experiments were calculated by dividing the slope uncertainty by the slope. These parameters were obtained following a method in Taylor (1982). As seen from the CV values listed in Table 1, individual experiments generally yielded well-defined  $D_o$ . Despite these well-defined individual  $D_o$  values, considerable variation was observed between individual experiments at a given temperature. Marrero and Mason (1972) have associated a 3% uncertainty with closed tube methods of  $D_o$  determination. Despite the scatter in the current  $D_o$  measurements, these results generally compare well with previously reported values as seen in Fig. 5.

Further comparisons between the present and previous work can be obtained by considering linear regressions of  $D_o(T)$  through the two sets of data. It should be noted that linear regressions of  $D_o(T)$  data are not strictly appropriate over large ranges in  $T$  since  $N_2$ - $O_2$  diffusivities are dependent on the Kelvin temperature as  $T^{1.724}$ . Nevertheless, scatter in the data on one hand, and the simplicity of comparing slopes and uncertainties on the other hand provide reasons for utilizing the linear regression. From inspection of the data from other studies shown in Fig. 5, it was decided to analyze this set of  $D_o(T)$  with and without inclusion of the apparently excessively low value at 25 °C due to the findings of Giddings and Seager (1962). Slopes of the linear regressions are 0.142 and 0.129  $mm^2 s^{-1} deg^{-1}$  for the previous data set with and without the Giddings-Seager data, respectively. Data from the present study yielded a slightly larger slope of 0.147  $mm^2 s^{-1} deg^{-1}$ . For further slope comparisons, the Marrero and Mason (1972) fit (Eq. [13]) yields a slope of 0.120  $mm^2 s^{-1} deg^{-1}$  when evaluated at 303 K (30 °C). At 30 °C, the linear regression-predicted  $D_o$  and uncertainties (following Taylor, 1982) are  $22.0 \pm 2.1$  and  $22.5 \pm 1.4 mm^2 s^{-1}$  with and without the Giddings-Seager data, respectively. The regression for the present study yielded  $22.9 \pm 1.2 mm^2 s^{-1}$  for  $D_o(30 °C)$ . The Marrero and Mason equation predicts a  $D_o$  at 30 °C of 21.4  $mm^2 s^{-1}$ . It should be noted that although Eq. [13] was generated from a set of diffusion data spanning a very wide range temperatures, only a very narrow temperature range from that set overlapped the temperature interval considered in the current work. Therefore, the most direct check on the present results appears to be through comparisons with the data in Table 2. From the linear regression parameters presented above, the current results are within the uncertainties of the earlier works.

Individual experiments for measuring  $D_o$  were fairly rapidly completed, generally taking about 30 min. Porous media effective diffusivity measurements usually required about 1 to 2 h per experiment. These latter measurements will be presented in a subsequent paper.

## SUMMARY

A new closed tube method for laboratory determinations of gas diffusivities was developed. The method was tested by measuring ordinary counter-diffusion of  $O_2$  in  $N_2$  at 0, 30, and 60 °C. Although individual experiments yielded well-defined diffusivities, scatter was observed between individual experiments at a given temperature. The measured diffusivities compared reasonably well with values previously reported in the literature. The method is suitable for measuring gas diffusivities in porous media. Results of measurements in various porous media will be presented in a subsequent paper.

## APPENDIX: EVALUATION OF EXPERIMENTAL TIME INTERVAL

Each diffusion experiment results in a full record of  $O_2$  concentrations as a function of time, but not all the data within a given experiment are useful in determining  $D_o$ . In particular, both short time as well as long time data were unusable. Only intermediate time data were useful in calculating diffusivities. Short time data could not be used because each experiment must be allowed to proceed into the time range where only the first term of Eq. [7] is significant. It is only after arriving in this time range that Eq. [9] and [11] can be applied to determine diffusivities. Though Crank (1975) does provide an analytic solution appropriate for short times, the well-stirred boundary condition is especially difficult to achieve during the beginnings of experiments when concentration gradients in the vicinity of  $x = L$  are substantial. The problem of instantaneously establishing a well-stirred boundary at  $t \approx 0$  is exacerbated with the use of the loop design for the measuring chamber. In this design, the rate of cycling of measuring loop gases must be greatly increased above the selected rate if the well-stirred condition is to be met at short times. Thus, relying on longer time data along with the previously mentioned equations necessitates some objective criterion for determining the time after which data are useful in calculating diffusivities.

There also exists an upper time limit within each experiment, after which data resolution limits the usefulness of applying Eq. [9] and [11]. This longer time limit arises as diffusive equilibrium is approached, and concentrations at various times become less distinguishable from the final equilibrium concentration. In terms of Eq. [9], the difference  $\Gamma(t) - B$  approaches zero, thus  $-\ln(\Gamma - B)$  approaches infinity. This large time behavior is not a mathematical limitation, since infinity is still approached linearly. The experimental limitation is actually due to finite resolution of all measurements used, especially the concentration readings.

### The Short Time Limit: The Approximate Time to Reach the Linear Region of $\ln[\Gamma(t) - B]$ vs. Time

A criterion for choosing times at which only the first term of Eq. [7] is needed to characterize  $\Gamma(t) - B$  is required. The criterion used for these experiments is due to Rolston (1986). Rolston's procedure is used in analyzing data from the method of Currie (1960), and it is directly transferable to the method used in this work.

Consider the first two terms in the summation in Eq. [7]. Let the first term in the series be  $Z$  times greater than the second term. This results in

$$\frac{\exp(-D_o \beta_1^2 t / \epsilon_g)}{L[\beta_1^2 + (\epsilon_g/a)^2] + (\epsilon_g/a)} \quad [A-1]$$

$$= \frac{Z \exp(-D_e \beta_2^2 t / \epsilon_g)}{L[\beta_2^2 + (\epsilon_g/a)^2] + (\epsilon_g/a)}$$

For  $Z \gg 1$ , only the first term in the series is significant, resulting in the linear time dependence of  $-\ln(\Gamma - B)$  and Eq. [11]. Rearranging Eq. [A-1] gives

$$\exp(D_e(\beta_2^2 - \beta_1^2)/\epsilon_g) = \frac{Z[L[\beta_1^2 + (\epsilon_g/a)^2] + (\epsilon_g/a)]}{L[\beta_2^2 + (\epsilon_g/a)^2] + (\epsilon_g/a)} \quad [\text{A-2}]$$

and

$$\tau_z = \frac{\epsilon_g}{D_e(\beta_2^2 - \beta_1^2)} \ln \left\{ \frac{Z[L[\beta_1^2 + (\epsilon_g/a)^2] + (\epsilon_g/a)]}{L[\beta_2^2 + (\epsilon_g/a)^2] + (\epsilon_g/a)} \right\} \quad [\text{A-3}]$$

where  $\tau_z$  is the time at which the first term in Eq. [7] becomes  $Z$  times greater than the second term.

For the set of diffusion experiments in this work,  $Z = 100$  provided adequate results (Fig. 4). After time  $\tau_{100}$ , plots of  $-\ln(\Gamma - B)$  were essentially linear with time. Substantially larger  $Z$  values would limit the usefully linear region of  $-\ln(\Gamma - B)$  vs. time. This limitation on increasing  $Z$  is due to  $\tau_z$  approaching or even exceeding upper time limits where measurement resolution contributes to errors.

### The Practical Upper Limit of $-\ln(\Gamma - B)$ vs. Time

Equations [7], [9], and [11] are in principle valid at all large times, however, resolution in measurements effectively constrain the useful time length for diffusion experiments. The nature of the upper time limit becomes apparent upon noting that

$$\lim_{t \rightarrow \infty} \frac{C_{so} - C(t)}{C_{so} - C_0} = \frac{a}{a + \epsilon_g L} \quad [\text{A-4}]$$

or equivalently,  $\Gamma(\infty) - B = 0$ . As this limit is approached, both gas analyzer accuracy and the accuracy of  $a$ ,  $\epsilon_g$ , and  $L$  measurements become critical. Noise and measurement errors are exacerbated at large times because diffusivities are obtained through taking the logarithm of differences, which approaches zero with time.

By applying error analysis to the quantities that comprise  $\Gamma - B$  (e.g., Taylor, 1982), an absolute uncertainty of about  $\pm 0.0023$  was obtained. Thus for  $-\ln(\Gamma - B) \geq -\ln(0.0023)$ , data become strongly influenced by measurement limitations. This corresponds to  $-\ln(\Gamma - B) \geq 3.77$ . A standard upper limit on experiment time was set at  $-\ln(\Gamma - B) = 3.5$ . The upper time limit associated with  $-\ln(\Gamma - B) = 3.5$  is designated  $\tau_{\max}$  (Fig. 4). Linear regression coefficients for analyses constrained within  $\tau_{100}$  on one hand, and  $-\ln(\Gamma - B) = 3.5$  on the other hand were quite high, supporting the choices of these criteria.

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